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PUBLICATIONS:

1. Theoretical Studies of Gas Phase Acidities and Stabilities of Pentacoordinated Silicon Anions, M.S. Gordon, L.P. Davis, L.W. Burggraf, and R. Damrauer, J. Am. Chem. Soc., 108, 7889 (1986).
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34. Hydride Abstraction from Siloles: Routes to Potentially Anti-Aromatic Species, P. Boudjouk, A.B. Rajkumar, J. Lambert, W. Schilf, M.S. Gordon, and K.A. Nguyen, Organomet., submitted.

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40. M.S. Gordon and L.A. Pederson, "Thermal Decomposition Pathways of Silanol", J. Phys. Chem., in press.

41. J.A. Boatz and M.S. Gordon, "Predicted Heats of Formation for Methyl-Substituted Disilanes", J. Phys. Chem., submitted.

42. J.A. Boatz, M.S. Gordon and L. Sita, "Theoretical Study of Metallocyclopropenes", J. Phys. Chem., submitted.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this research has been to use state-of-the-art methods in electronic structure theory and dynamics to develop an understanding of a variety of problems in the chemistry of silicon and related elements of particular importance to the Air Force. The problems of interest include: studies of precursors of materials and coatings; studies of the mechanisms for polymerization of silicic acid, including an elucidation of the role of hypervalent anionic silicon in this mechanism; elucidation of interactions of drying agents with silicic acid and related species; analysis of the potential mechanisms for chemical vapor deposition of silicon, starting from silane and substituted silanes. A broad study of anionic pentacoordinated silicon compounds has been completed, demonstrating that the most effective ligands for stabilizing such species are electronegative groups from the first or second periods in the periodic table. Third period elements (e.g., Cl, SH) are much less effective. Since these hypervalent species can be stabilized by as much as 30 kcal/mol, the pseudorotation of the ligands in the manner proposed by Berry can play an important role in the dynamics of nucleophilic reactions at silane centers. For this reason we have developed an accurate potential energy surface to describe the pseudorotation motion, as a first step in gaining an understanding of the dynamics of the overall process. This was also the first complete theoretical verification of the Berry pseudorotation process. Studies have also been performed on several hexacoordinated dianions of silicon. When the ligands are electronegative, it is found that these species are quite stable, both to loss of one ligand and to loss of an electron, even though the hexacoordinated species are thermodynamically unstable relative to their pentacoordinated counterparts. Several experiments have also demonstrated the existence of neutral pentacoordinated compounds, most notably the silatranes. As a first step in the theoretical study of such species, we have carried out a systematic analysis of neutral pentacoordinated silicon compounds of the type $X-SiY_3-NH_3$. We have found that when $Y=F$ and $X=F$ or Cl , these compounds are quite stable, with dissociation energies of 10 kcal/mol or more.

In the area of chemical vapor decomposition, we have completed detailed studies of several small silicon hydrides. These include silylene, disilane, methylsilane, dimethylsilane, ethylsilane, trisilane, disilylmethane, and silanol. In general, the decompositions of these compounds in their electronic ground states occur primarily via molecular, rather than radical, eliminations, with the most common products being molecular hydrogen and silylene. Usually, 1,1- H_2 elimination is preferred over 1,2- elimination, although this is reversed in silanol. The energetics of the interconversion and dissociation of the isomers of disilyne have also been investigated on both the ground singlet electronic state and the lowest triplet state.

AFOSR FINAL REPORT

THEORETICAL STUDIES OF SILICON CHEMISTRY

AFOSR 87-0049

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I. INTRODUCTION

In the following pages, the work carried out under AFOSR grant 87-0049 is summarized. The summary is presented by category. Within each category, the title indicates whether the work has been completed (manuscript in preparation, submitted, in press, or published) or the research is still in progress. In either case, a summary of further work to be performed is given. This is the final report for this grant.

II. IONS

A. Theoretical Studies of Gas Phase Acidities and Stabilities of Pentacoordinated Silicon Anions, M.S. Gordon, L.P. Davis, L.W. Burggraf, and R. Damrauer, J. Am. Chem. Soc., 108, 7889 (1986).

This work was the first in a series of investigations of the structure and stability of pentacoordinated silicon-containing anions and of the role that some of these anions may play in silanol polymerization mechanisms. All of these studies are combined ab initio/MNDO investigations. The gas phase acidities were calculated with a range of basis sets and computational levels, including state-of-the-art calculations with extended basis sets and full fourth order perturbation theory (MP4). The latter predict experimental gas-phase acidities with an accuracy of 2 kcal/mol. Importantly, reducing the computational level to MP2/6-31++G(d,p) does not seriously diminish the computational accuracy. Thus, subsequent calculations on the larger molecules were performed with at the latter level. The ab initio calculations predict stable pentacoordinated structures for the anions XSiH_4^- (X=H, CH₃, NH₂, OH, F), with the latter four substituents about the same in stability (roughly 30 kcal/mol relative to $\text{SiH}_4 + \text{X}^-$) and about 15 kcal/mol more stable than H. In contrast, the third period substituents (SiH₃, PH₂, SH, Cl) are predicted to be only marginally stable and appear to form weak charge-dipole complexes, rather than trigonal bipyramidal pentacoordinated compounds.

B. Theoretical Study of the Decomposition of Five Coordinate Silicon Anions, L.W. Burggraf, L.P. Davis, and M.S. Gordon, J. Am. Chem. Soc., 110, 3056 (1988).

In this work the stabilities of the title compounds relative to a variety of decomposition products are studied with ab initio (MP2/6-31++G(d,p)) and MNDO calculations. The decomposition reactions may be divided into two types: elimination of an anionic substituent (e.g., OH⁻, H⁻, CH₃⁻) and the elimination of a neutral molecular compound (e.g., H₂, H₂O, CH₄). The former reactions tend to proceed with a monotonic increase in energy, while the latter typically encounter energy barriers and have products which may be either higher or lower in energy than the parent anion. Both ab initio and MNDO calculations predict that removal of methane from the pentacoordinated structure is likely, via a transfer of the OH proton to an adjacent methyl substituent. The ab initio calculations predict that this process is 25 kcal/mol exothermic with a barrier of 16 kcal/mol for the monomethyl compound and 40 kcal/mol exothermic for the tetramethyl compound. In contrast, MNDO predicts the monomethyl process to be slightly endothermic and the tetramethyl methane elimination to be slightly exothermic with a 21 kcal/mol barrier. The ab initio calculations also find that the elimination of H₂, with one hydrogen coming from Si and the other from OH, has a small (10 kcal/mol) barrier and a 20 kcal/mol exothermicity. In contrast, water and methanol elimination are predicted by MNDO to have very high barriers of 96 and 104 kcal/mol, respectively, in the monomethyl compound and 70 and 78 kcal/mol in the tetramethyl case.

C. Gas Phase and Computational Studies of Pentacoordinate Silicon, R. Damrauer, L.W. Burggraf, L.P. Davis, and M.S. Gordon, J. Am. Chem. Soc., 110, 6601 (1988).

This work is the result of a combined study using the flowing afterglow (FA) experimental technique and ab initio and semi-empirical electronic structure calculations to investigate the stability of a wide variety of pentacoordinated

silicon anions. The compounds studied have the general formula SiH_3XY^- , and the general reaction of interest is:



A key question here is whether the initial formation of the pentacoordinated species occurs with more or less excess energy than is required for the subsequent dissociation. That is, is the initial reaction more or less downhill than the final reaction is uphill? If the exothermicity on the left is smaller than the endothermicity on the right, then it should be possible to isolate the pentacoordinated species in the FA. Of the 91 species studied, all but five are predicted to be stable relative to loss of an anion (X^- or Y^-), and as a result of the study many previously unreported siliconates have been prepared and studied in the FA. Most impressively, there is very close agreement between those compounds predicted to be stable by the calculations and the experimentally observed stability. This lends considerable confidence to the predictive capability of theory. The ab initio and semi-empirical calculations are generally in good qualitative agreement, although the relative stabilities for X or $\text{Y} = \text{F}$ are not predicted correctly at the semi-empirical level.

D. Structure and Stability of Hexacoordinated Silicon Dianions, M.S. Gordon, L.P. Davis, and L.W. Burggraf, J. Am. Chem. Soc., submitted.

While it is now well established that pentacoordinated silicon anions can be quite stable, especially when the ligands are chosen from the first or second period, it is not clear whether hexacoordinated dianions are stable relative to the pentacoordinated species. If they are, this would have important implications for mechanisms of formation of siliconates and related compounds and may point the way to useful energetic materials. We have therefore performed a combined semi-empirical/ab initio study of several hexacoordinated with the formula SiX_6^{2-} , with $\text{X} = \text{H}, \text{CH}_3, \text{OH}, \text{F}, \text{Cl}$. The energetics for the reaction

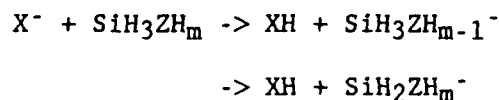


have been studied at the semi-empirical level for all ligands X and at the ab initio level for X=H and F.

For hydrogen, MP2/6-31++G(d,p)//HF/6-31++G(d) calculations predict the above reaction to be 84.1 kcal/mol exothermic, but there is a 3.1 kcal/mol activation energy for the dissociation. The corresponding AM1 results are 115.1 and 23.4 kcal/mol, so the semi-empirical calculations predict too large an exothermicity and too large an activation barrier, but the two sets of results are in qualitative agreement. For X=F analogous ab initio calculations predict the dissociation of SiF_6^- to be 44.7 kcal/mol exothermic, while the AM1 reaction is 78.3 kcal/mol down hill. Both levels of theory predict the hexacoordinated compound to be a minimum on the potential energy surface, and AM1 predicts an activation energy of 62.2 kcal. The latter value is likely to be too high. For X=Cl, OH, and CH_3 , AM1 predicts exothermicities 48.3, 59.5, and 92.1 kcal/mol, respectively, and activation energies of 32.4, 26.0, and 17.0 kcal/mol. A particularly interesting result of the ab initio calculations is that d orbitals are not found to play a major role in the hypervalent compounds. This provides at least a partial explanation for the qualitative success of the semi-empirical calculations.

E. Potential Energy Surfaces for the Attack of H^- , OH^- and NH_2^- on Methylsilane, D.R. Gano, M.S. Gordon, L.P. Davis, and L.W. Burggraf, work in progress.

Related to the foregoing calculations is the detailed investigation of the potential energy surfaces for the reactions



Of particular interest are $\text{ZH}_m = \text{CH}_3$ and $\text{X}^- = \text{H}^-$, OH^- and NH_2^- . The results of this analysis has important implications for the relative stabilities of the two product isomers and for the relative barrier heights of the two processes.

Indeed, theory predicts that $\text{SiH}_2\text{CH}_3^-$ is 15 kcal/mol more stable than $\text{SiH}_3\text{CH}_2^-$

with a substantial barrier separating the two isomers, while there is experimental evidence that the former isomer is more difficult to produce (i.e., there may be a higher barrier). The two reactions may proceed in many different ways, including direct abstractions or initial formation of a pentacoordinated intermediate followed by elimination of XH. The calculations will be very useful in helping to unravel the mechanism. For H^- , we have established that a barrier exists for the direct abstraction at the Si end. The search for the transition states for the other routes is under way. For NH_2^- , the transition states for the direct abstractions have been found, and those for the internal abstractions from pentacoordinated intermediates are under investigation.

F. Mechanism of Formation of Polysiloxanes, L.W. Burggraf, L.P. Davis, M.T. Carroll, and M.S. Gordon, research in progress.

The main pentacoordinated species of interest here is $Si(OH)_5^-$, and the calculations of interest are to determine the stability of this species relative to various decomposition products, including $Si(OH)_4 + OH^-$ and $Si(OH)_3O^- + H_2O$, as well as the structures and energies of the associated transition states. We have already calculated the MP2/6-31++G(d,p) relative energies at the AM1 geometries, and the RHF/6-31G(d) structures have been determined. Currently in progress are the verification that all structures are minima on the potential energy surface. This will be followed by the calculation of MP2/6-31++G(d,p) single point energetics. Also in progress is the study of the effect on the energetics of adding water molecules to the reaction.

The next phase of this project will be to investigate the interactions of other substrates with silicic acid. These will include water (to study hydrogen bonding), and HF, NH_3 , and formamide (to simulate the effects of drying agents). The approach will be analogous to that described in the previous paragraph.

G. Gas Phase Acidities, M.S. Gordon, D.R. Gano, and D. Volk, J. Phys. Chem., in press.

Still another aspect of this problem is the effect of substituents on XH_n gas phase acidities. Structures have now been determined at the RHF/6-31G(d) computational level for the compounds $XH_{n-1}Y$, and their associated anions $XH_{n-2}Y^-$, where $X=C, N, O, Si, P, S$, and $Y=CH_3, NH_2, OH, F, SiH_3, PH_2, SH$, and Cl . The gas phase acidities have been determined with 4th order perturbation theory and an extended basis set. For methylsilane, the only compound for which the gas phase acidity is known experimentally, the theoretical value is within the experimental error bars.

H. Theoretical Studies of the Reactions of Si_n^+ with Methylsilane, L.P. Davis, L.W. Burggraf, K. Nguyen, and M.S. Gordon, research in progress.

In a recent experimental paper, Bondybey and co-workers reported a FT-MS study of the reactions of cationic silicon clusters with methylsilane. The experiments were only able to determine the molecular formulas of the products. Since there are a very large number of possible products, even for $n=1$, and since there are many isomeric forms for most of the products, we have embarked on a combined ab initio/MNDO study of the possible reactions, with particular interest in determining the relative thermodynamics and barrier heights for the competing reactions. Several possible products of the reaction $Si^+ + CH_3SiH_3$ are predicted to be formed with release of energy at the MP2/6-31G(d) level of theory. These include (exothermicities in parentheses) $H_2CHSiH_2^+ + H$ (5.9 kcal/mol), $SiCH_3^+ + SiH_3$ (4.7), $SiH_2CH_2Si^+ + H_2$ (20.7), $H_3SiCHSi + H_2$ (5.0), $H_3SiSiCH_3^+$ (45.2), $SiHSiH_2CH_3^+$ (38.3), $SiH_3CH_2SiH^+$ (46.0), $SiH_2SiHCH_3^+$ (53.5), $SiH_2SiH_2CH_2^+$ (47.0). The remaining products are predicted to be uphill in energy. In collaboration with Dr. Raghavachari at Bell Laboratories, several transition states have been identified. Because of the complexities of the transition states and the reactions themselves, it is not entirely clear which reactant/product pairs are connected by which transition states. To unravel this complex reaction network, we are now proceeding to generate the reaction paths for all interesting reactions.

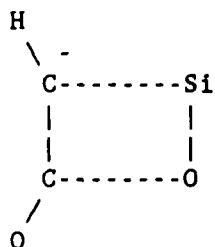
I. Theoretical Studies of HCSi^- and H_3CSi^- , M.W. Schmidt and M.S. Gordon, research in progress.

In a recent flowing afterglow selected ion flow tube (FA-SIFT) experiment, Damrauer and Depuy have subjected methylsilane to electron bombardment. The decomposition products of this reaction have been observed, and the reactions of certain of these products with other species have been investigated. Virtually all possible breakup products are observed, including SiH_x^- ($x=0-3$) and SiCH_x^- ($x=0-5$). Of particular interest are the structures of SiCH^- and SiCH_3^- and their reactivity (or lack thereof) with CO_2 , SO_2 , CH_3OH , O_2 , and other substrates. These reactions have been studied in the FA-SIFT experiments.

Our RHF/6-31G(d) calculations find SiCH^- to be linear, with the hydrogen attached at carbon. No other minimum has been found on the potential energy surface; linear HSiC^- has a doubly degenerate imaginary frequency.

For SiCH_3^- , both planar structures ($\text{H}_2\text{C}=\text{SiH}^-$ and $\text{H}_2\text{Si}=\text{CH}^-$) are found to be minima on the potential energy surface, with the former lying 38 kcal/mol below the latter at the MP2/6-31++G(d,p) level of computation. These relative energies may be explained in terms of the greater stability of CH, relative to SiH, bonds. The isomerization connecting the two isomers occurs through a nonplanar transition state which is 75 kcal/mol above the global minimum at the same level of theory.

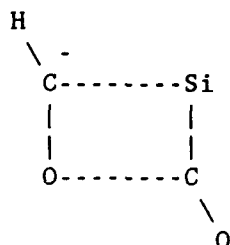
In the reaction of HCSi^- with CO_2 , the observed products are $\text{HCCO}^- + \text{SiO}$. This has been interpreted in terms of a 4-center transition state,



Most of the other reactions which HCSi^- and H_3CSi^- undergo can be rationalized in terms of similar 4-center transition states. An investigation of the

reaction surface for $\text{HCSi}^- + \text{CO}_2$ has been initiated in this laboratory. It is somewhat surprising that the proposed 4-center transition state is in fact a minimum on the potential energy surface (PES), as verified by the fact that the matrix of second energy derivatives (hessian) is positive definite. Furthermore, this cyclic structure appears to be the global minimum on the PES, being much lower in energy than either reactants or products. So far, no transition state separating either reactants or products from this global minimum has been found. A systematic search for such a transition state has not been completed, however.

A second planar 4-center species,



is also found to be a minimum, albeit 61 kcal/mol above the former structure and 2 kcal/mol above the reactants at the MP2/6-31++G(d,p) level of theory. The first structure is the more stable due to the existence of the very strong SiO bond. Because these structures are potential energy minima, they represent intermediates, rather than transition states, on the potential energy surface. The transition state connecting the reactants to the second (higher energy) intermediate has been located at 9 kcal/mol above the reactants. Similar results have now been obtained for the reaction of HCSi^- with CS_2 , SO_2 , and OCS .
 J. Pseudorotation in Pentacoordinated Silicon Compounds, M.S. Gordon, T.L. Windus, L.P. Davis, and L.W. Burggraf, J. Am. Chem. Soc., in press.

One of the motions that a pentacoordinated structure can undergo is Berry pseudorotation. Here, one of the three equatorial ligands (the pivot group) is held fixed, while the other two equatorial groups exchange positions with the axial ligands. This motion is very important for pentacoordinated silicon

anions, because these anions can be quite stable with 15-30 kcal/mol potential energy wells. Therefore, if the barriers to the pseudorotational motion are relatively small, the molecule might be able to pseudorotate into several different structures prior to dissociation. This is expected to have profound consequences on the stereochemistry of the S_N2 reactions of silanes.

To investigate this phenomenon, we have initiated a combined electronic structure/dynamics investigation of pseudorotation in $SiH_nF_mCl_p^-$ compounds ($n+m+p=5$). The simplest compound is the parent SiH_5^- . For this species, the pseudorotation barrier is predicted to be about 2 kcal/mol, whereas the depth of the well for adduct formation is 15 kcal/mol. Therefore, the pentacoordinated structure can, in principle, pseudorotate several times before dissociating. We are now evaluating the minimum energy path for the pseudorotational motion, as the first step for a study of the dynamics of this process. The latter will be performed in two ways: using variational transition state theory (VTST) and by investigating classical trajectories. The classical trajectory investigations will allow us to determine the vibration-vibration energy transfer probabilities between the S_N2 and pseudorotation reaction paths and therefore the efficiency of energy transfer between the two reaction coordinates.

The pseudorotation barriers for several F- and Cl-substituted compounds have now been determined as well. It is found that electronegative substituents increase the barriers for pseudorotation from the global minima. However, these minima are also much deeper than for SiH_5^- , so there is still ample opportunity for pseudorotation prior to dissociation.

K. Decomposition of $CH_3SiH_2^+$, L. Pederson, K. Nguyen, and M.S. Gordon, research in progress.

It has been discovered in FT/MS experiments that the thermodynamically most stable decomposition product of $CH_3SiH_2^+$, CH_3Si^+ , is not observed, while the other two isomers are found in roughly equal amounts. This curious result is

most likely due to the existence of larger energy barriers to the decomposition at the silicon end. In order to unravel this mystery, we have begun a series of calculations on the transition structures and energetics for formation of the three isomers of CSiH_3^+ . Preliminary calculations suggest that the three barriers are indeed much closer to each other than the thermodynamics would suggest, and much more sophisticated calculations with larger basis sets and correlation corrections are in progress.

L. Photoionization Cross Sections of Methane and Silane, S. Koseki and M.S. Gordon, research in progress.

The photoionization cross sections of SiH_4 and its daughter cations are quite different from the analogous pattern for methane. In the latter case, the peaks in the spectrum simply correspond successively to CH_n^+ , with n decreasing from 4 to 1. Because of the unusual stability of SiH_2^+ , however, this species exhibits an anomalous behavior in the silane photoionization. Our calculations correctly reproduce the essential features of the silane vs. methane photoionization spectra. An additional possible difference between the two molecules is the potential existence of barriers to the dissociations of the SiH_n^+ ions, and we are currently searching for the corresponding transition states.

III. REACTION SURFACES

A. Theoretical Study of the Lowest Triplet Potential Energy Surface of Si_2H_2 , S. Koseki and M.S. Gordon, J. Phys. Chem., 92, 364 (1988).

As part of a comprehensive investigation of reactions which may be important in chemical vapor deposition (CVD), we have embarked on a study of the singlet and triplet potential energy surfaces of disilyne.

Binkley had determined that there are two minima corresponding to a bent $^3\text{A}''$ silasilene structure (with the planar triplet apparently the transition state for the inversion motion) and a twisted ^3B disilyne. However, the addition of

zero point vibrational energies to his results reverses the energy order of the bent and planar silasilene structures. Our more extensive calculations verify this result, and we predict the minimum to be planar, rather than bent. This C_{2v} structure is predicted to be the global minimum on the triplet potential energy surface. The second Binkley minimum, obtained with unrestricted Hartree-Fock (UHF) wave functions, is also questionable, since this state is UHF unstable. Also, at the MP4/6-31++G(d,p)//UHF/6-31G(d,p) level both planar cis and trans disilyne are found to be more stable than the twisted form found by Binkley. Unfortunately, the UHF wave functions for the two planar structures are also unstable. This suggests that a multiconfigurational approach is needed. At the FV MCSCF/6-31G(d,p)//MCSCF(4,4)/6-31G(d,p) level of computation, trans planar disilyne is indeed found to be lower in energy than the nonplanar structure. The potential energy surface for the rotation about the Si-Si bond has also been investigated using MCSCF wave functions, revealing the existence of three local minima: the cis-bent (C_s), twisted (C_2), and trans-bent (C_{2h}) structures. The rotation barrier from trans-bent to cis-bent is about 11 kcal/mol, while there is only a small barrier between the cis-bent and twisted structures. The latter might disappear at higher computational levels, because it is caused by a strong avoided crossing with a higher electronic state, and external correlation may be important.

B. Theoretical Study of the Singlet Potential Energy Surface of Si_2H_2 , S.

Koseki and M.S. Gordon, J. Phys. Chem., 93, 118 (1989).

The pertinent reactions on the singlet surface include the isomerization of disilyne to silasilene and the dissociation of both isomers to $Si_2 + H_2$. At the RHF/6-31G(d,p) level, the transition state for the isomerization from planar singlet silasilene to the global Si_2H_2 minimum bridged disilyne is planar with one partially formed Si-H-Si bridge bond formed by the attack of one of the two Si-H bonds on the empty 3p orbital of the terminal silicon of silasilene. The

MP4(SDQ)/6-31G(d,p) barrier for the reaction is only 4.1 kcal/mol. An MCSCF/6-31G(d,p) calculation with 7 active orbitals and 6 active electrons yields a similar value of 5.3 kcal/mol. The reverse barrier is found to be 14.7 and 7.1 kcal/mol, respectively, by the two methods. Since there is relatively little configurational mixing on this part of the surface, it is expected that the MP4 results are more accurate. Analysis of the vibrational frequencies along the reaction path has provided the necessary input for the calculation of the free energy path for the isomerization. This is particularly exciting, since it allows the prediction of temperature effects on the energetics. According to these calculations, the minimum at the higher energy isomer (silasilene) may disappear at higher temperatures.

Extensive calculations at the full valence (FV) MCSCF/6-31G(d,p) level apparently detect a transition state leading from bridged disilyne to $\text{Si}_2 + \text{H}_2$, with a barrier of 43.8 kcal/mol. A long range minimum is also detected on this surface, at a 2.42 Å separation of the two fragments. The barrier for the dissociation is only 1.9 kcal/mol higher than this long range minimum, so the latter may disappear at higher computational levels.

The C_{2v} (least motion) path leading from planar silasilene to $\text{Si}_2 + \text{H}_2$ is symmetry forbidden. Because large configurational mixing is expected along this reaction path, the C_s transition state has been determined at the (7 orbital, 6 electron) MCSCF level; however, because the calculation is complicated by a bifurcation that occurs along this path, so that an intrinsic reaction coordinate (IRC) calculation cannot in itself identify the reactants and products connected by this transition state. More extensive calculations on this surface are under way.

The alternative dissociation of silasilene to $\text{SiH}_2 + \text{Si}$ has also been investigated using an MCSCF(6,6)/6-31G(d,p) wave function. It is found that the barrier for this reaction is much larger than that for the isomerization to bridged disilyne, so the latter is probably the preferred path.

C. Reactions of Atomic Silicon With Water, S. Sakai, M.S. Gordon, and K.D. Jordan, J. Phys. Chem., 92, 7053 (1988).

The interactions of silicon atoms and water molecules have been studied in a solid argon matrix at 15K by Ismail et al (J. Chem. Phys., 77, 1617 (1982)).

These authors propose the following mechanism for the formation of ^1SiO and $^1\text{H}_2$:
 $\text{Si}(^3\text{P}) + \text{H}_2\text{O} \rightarrow \text{Si}:\text{OH}_2(^3\text{A}_2) \rightarrow \text{HSiOH}(^3\text{A}'') \rightarrow \text{HSiOH}(^1\text{A}') \rightarrow ^1\text{SiO} + ^1\text{H}_2$

This suggests that the singlet-triplet spin-orbit coupling-induced intersystem crossing occurs at the HSiOH compound. A major objective of this work has been to analyze the singlet and triplet surfaces in order to determine where the singlet-triplet crossing is most likely to occur. The calculations were carried out with the 6-31G(d) basis set and both MP4 and MCSCF wave functions, and the intrinsic reaction coordinate (IRC) was used to compare the reaction paths. Our analysis suggests that the singlet-triplet crossing occurs near the singlet transition state and before the (higher energy) triplet transition state, so the intersystem crossing occurs before the system needs to traverse the higher energy barrier. We have also calculated the energy requirements for the elimination of molecular hydrogen from both H_2SiO and cis HSiOH. The former reaction is predicted to be exothermic by 3.7 kcal/mol, but it has a large 92 kcal/mol barrier. The latter reaction has a 53.4 kcal/mol barrier and is nearly thermoneutral.

D. Reactions of Atomic Carbon and Silicon With Methane and Silane, S. Sakai and M.S. Gordon, J. Phys. Chem., 93, 1884 (1989).

The potential energy surfaces for the reactions of both singlet and triplet carbon and silicon atoms with methane and silane have been calculated with MP4, 6-31G(d,p) wave functions. The singlet atoms tend to insert into the X-H bonds to form methylenes or silylenes, while both insertion and abstraction transition states can be found on the triplet surfaces. Because the abstraction surfaces must be treated with MCSCF wave functions, this first paper deals only

with the insertion reactions. A later paper will deal with the abstractions.

The activation energies for the insertions of singlet carbon into methane and silane are 6.1 and 4.7 kcal/mol, respectively. These may be compared with the zero barriers for the analogous insertions of methylene into the same bonds. The difference is very likely that the formation of carbenes in the atom insertions is not favorable. The activation energies for the insertions of singlet silicon into methane and silane are 12.6 and 1.1 kcal/mol, respectively, as compared with 21 kcal/mol and zero for the corresponding silylene insertions. The activation energies for the insertions of triplet carbon into methane and silane are predicted to be 30.6 and 0.0 kcal/mol, respectively, while the insertion of triplet silicon into silane requires 7.3 kcal/mol. We have so far been unable to find the transition state for the insertion of triplet silicon into methane, and we suspect that this transition state may actually merge with the abstraction transition state. Further investigations are being carried out on this surface.

E. Vibrational Dependence of the Lowest Electronic Transition in Disilene, S. Koseki and M.S. Gordon, J. Phys. Chem., submitted.

This is a study of the dependence of the energy difference and the transition dipole moment between the ground state and the singlet ($\pi \rightarrow \pi^*$) state on motions along some of the normal modes (Q_i) in Si_2H_4 , in an attempt to understand the vibrational structure of the UV spectrum of this molecule. Since the lowest ($\pi \rightarrow \pi^*$) and ($\sigma \rightarrow \sigma^*$) states are very close to each other in energy and belong to the same irreducible representation, the approach we are taking is to use MCSCF + CI wave functions to determine the Q-dependence of the vertical excitation energy and transition moment. The particular vibrational motions of interest are rotation about the Si-Si bond and flapping of the SiH_2 groups.

As expected, it is generally found that Si_2H_4 is a much "floppier" molecule than ethylene. Rotation about the central X-X bond is much easier for X-Si than

for X=C. The same is true for the flapping of the XH_2 groups. Because internal rotation partially breaks the pi bond and therefore destabilizes the ground state, both motions decrease the excitation energy to the first excited state. What is not so obvious is that the oscillator strengths for both molecules and for both types of distortion have their maxima at the planar structure.

We are now generating cubic splined potential energy curves and adding to the GAMESS code the capability to calculate Fourier-expanded wavefunctions and Franck-Condon factors from cubic splined transition dipole moments.

F. The Reaction of SiH_2 With O_2 , S. Koseki and M.S. Gordon, research in progress.

The first step in this study has been to determine the minima on the singlet and triplet potential energy surface of O_2SiH_2 . At the RHF/3-21G* level of theory, seven such singlet minima with positive definite force fields have been found, the lowest energy isomer being dihydroxysilylene, $\text{Si}(\text{OH})_2$. The lowest of the six triplet UHF/3-21G* minima has the same structure and is predicted to be 50 kcal/mol higher in energy than the lowest singlet. The large singlet-triplet splitting for $\text{Si}(\text{OH})_2$ is consistent with previous calculations on SiF_2 . The next steps in this problem are to re-examine the minima with MCSCF wave functions and then to study the potential energy surfaces for the dissociation and isomerization reactions.

G. Insertions of SiH_2 and CH_2 into Heavy Atom Bonds, D.R. Gano and M.S. Gordon, J. Am. Chem. Soc., in press.

We have shown in earlier papers that whereas the insertion of methylene into the C-C bond of ethane must overcome a large (more than 40 kcal/mol) energy barrier, the analogous insertion into the strained C-C bond of cyclopropane occurs with a much smaller 2.2 kcal/mol barrier. The latter is only marginally larger than the insertion into a C-H bond of ethane. Similar calculations on the insertions of CH_2 and SiH_2 into the C-Si bond of silacyclopropane and the

Si-Si bond of disila cyclopropane are similarly much smaller than the corresponding insertions into the C-Si and Si-Si bonds of methylsilane and disilane, respectively. Insertions into the unstrained heavy atom-heavy atom bonds are much larger than the insertions into the corresponding bonds to hydrogen, whereas, the insertions into the ring bonds are very small or non-existent.

H. $^3\text{O} + \text{HCl}$, M.S. Gordon, K.K. Baldrige, R.J. Bartlett, and D. Bernholdt, Chem. Phys. Lett., 158, 189 (1989).

This is a project suggested by the experimental work of R.N. Zare, the key question being the structure of the transition state. At the MP2/6-31G(d,p) MCSCF/6-31G(d,p), and coupled cluster levels of theory, the transition state is predicted to be bent, with an angle of 135° . The energetics of the reaction has been predicted at several levels of theory. It is found that the predicted barrier heights are sensitive to the basis set used. At MP4(SDTQ)/MC-311G(2df,2pd)//MP2/MC-311G(d,p) level of theory, the forward and reverse barriers are calculated to be 14.6 and 12.8 kcal/mol, respectively. The corresponding activation energies are 12.6 and 9.8 kcal/mol, respectively. SAC corrections lower the activation energies even further, as do the coupled cluster calculations.

We have also generated the MP2/6-31G(d,p) minimum energy path for the reaction and generated the bend potential orthogonal to the reaction path at many points along the path. On the minimum energy path, as the oxygen atom approaches, the angle begins to decrease. It continues to decrease through the transition state and on toward products. These results agree with the experimental observation that the product OH produced is rotationally hot. We have now entered into collaborative efforts with George Schatz (Northwestern University). This collaboration will result in the construction of an analytical PES for the reaction, which will then be used to study the dynamics of the reaction using quantum trajectory studies. Analogous calculations to

those described above have also been initiated on the reaction $O + HBr \rightarrow OH + Br$. The MP2/3-21G(d,p) transition state for this reaction is also bent. We are now proceeding to develop larger basis sets for Br, so that calculations can be performed at levels comparable to those described above for Cl. Calculations will also be initiated shortly on the reaction $O + SiH_4 \rightarrow OH + SiH_3$.

I. The Dissociation of F_2 , M.S. Gordon and D.G. Truhlar, Theoret. Chim. Acta, 71, 1 (1987).

It has been known for some time that the dissociation of F_2 is not treated properly at the Hartree-Fock level of theory. Indeed, at this level, two fluorine atoms are found to be lower in energy than F_2 . What was not known was whether the potential energy surface contains local minima or maxima. This work demonstrated, using very large basis sets, that the best Hartree-Fock potential energy surface for F_2 is purely dissociative.

K. Isomerization of Silaethylene, R.S. Grev, G.E. Scuseria, A.C. Scheiner, H.F. Schaefer III, and M.S. Gordon, J. Am. Chem. Soc., 110, 7337 (1988).

Previous papers from this and other laboratories have pointed out that silaethylene is slightly (1-3 kcal/mol) lower in energy than its isomer methylsilylene. It came as quite a surprise, therefore, when a joint experimental-theoretical paper by Goddard and Beauchamp appeared in which the energy difference is claimed to be 10 kcal/mol. Our group then joined with the Schaefer group to carry out much higher level calculations than used previously to settle this issue. With very large basis sets, MP4 (SDTQ), CI, and coupled cluster calculations all predict the energy difference to be 1-3 kcal/mol, as originally believed. Our joint work also corrects errors in the Beauchamp-Goddard paper regarding the internal rotation in silaethylene and the singlet-triplet splitting in carbenes and silylenes.

L. Internal Rotation in 1-Silabutadiene, M. Steinmetz, B.S. Udayakumar, and M.S. Gordon, Organomet., in press.

Experimental photochemistry performed at Marquette University (Steinmetz, Udayakumar) suggests that the barrier separating the two stable forms of 1-silabutadiene is large enough that the less stable "cis" isomer may be implicated in the photochemical mechanism. To investigate this, we have initiated calculations on the internal rotation of this molecule about its central CC bond. It has been discovered that the planar cis structure is not a minimum and that the second minimum, if it exists, must be a twisted structure. Indeed, there has existed for some time considerable controversy regarding the structure of the second minimum in 1,3-butadiene itself. No definitive calculation had been performed to resolve this question until our calculations showed the second minimum to be gauche with a rotational angle of about 40°. We are now proceeding to determine the structure of the second minimum and associated barrier heights in the silicon-substituted compound.

M. The Molecular and Electronic Structure of SiN₂, M.S. Gordon, research in progress.

The lowest singlet and triplet potential energy surfaces of SiN₂ are under investigation, in collaboration with Dr. Alan Garscadden at Wright-Patterson AFB. This compound can exist as either NSiN or SiNN. On the singlet surface, a stable C_{2v} ring structure with a 40.2° NSiN angle has been found at the RHF/6-31G(d) level of computation, while all attempts to locate a stable SiNN structure lead to dissociation to Si + N₂. On the triplet surface, the C_{2v} ring structure is a transition state with one imaginary frequency. Following the normal mode corresponding to the downhill direction leads to ground state silicon + N₂. Thus, no stable triplet SiN₂ has yet been detected. In order to gain a better understanding of the potential energy surfaces of this compound, extensive MCSCF calculations have been initiated for this system.

N. Transition State Structure, Barrier Height, and Vibrational Frequencies for the Reaction Cl + CH₄ -> CH₃ + HCl, T.N. Truong, D.G. Truhlar, R. Steckler, K.K. Baldrige, and M.S. Gordon, J. Chem. Phys., 90, 7137 (1989).

Very large basis sets and second order perturbation theory with SAC corrections have been used to predict the structure, barrier height, and vibrational frequencies for the reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$. This is expected to be the most accurate ab initio calculation for these properties for a polyatomic molecule.

IV. THEORY AND MODEL DEVELOPMENT

A. Algorithms and Accuracy Requirements for Computing Reaction Paths, K.K. Baldridge, M.W. Schmidt, D. Bartol, B.C. Garrett, M.J. Redmon, R. Steckler, D.G. Truhlar, and M.S. Gordon, J. Phys. Chem., 92, 1476 (1988).

Recent advances in electronic structure theory allow the direct computation of gradients, and sometimes higher derivatives, of potential energy surfaces with only a small increase in computational effort over the calculation of the energy itself. This development has led to increased interest in minimum energy paths (MEP's, sometimes referred to as intrinsic reaction coordinates or IRC's) computed by the method of steepest descents and in using these paths as a first step in the prediction of reaction dynamics. This work was initiated to address the question of the accuracy with which the reaction path must be calculated, for a given level of electronic structure theory, in order to converge the calculation of the IRC and of thermal rate constants based on reaction paths and reaction path potentials. To this end, both ab initio and empirical potential energy surfaces have been used. The ab initio surfaces are those for the reactions $\text{HCN} \rightarrow \text{HNC}$ and $\text{H}_2 + \text{CH}_3 \rightarrow \text{H} + \text{CH}_4$, both computed with HF/STO-3G wave functions. The empirical surfaces are for the latter reaction and for $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$.

Several algorithms have been used to compute the reaction paths. The simplest approach is the simple gradient-following method. Here, an initial step off the saddle point is taken in the direction of the normal mode corresponding to the imaginary frequency. Subsequently, small steps are taken

in the direction of the negative of the gradient (either toward reactants or toward products) in mass-weighted or mass-scaled cartesian coordinates. More sophisticated algorithms which take advantage of the knowledge of previous energies and gradients can also be devised. Those tested in the current work are the n th order Adams-Moulton method with either fixed (FAM) or variable (VAM) step sizes and the fixed-step-size Adams predictor method (FAP). The FAP method of order zero (FAP0) is identical to the simple gradient-following method described above, and FAP1 is equivalent to a quadratic fit of the surface using two previous gradients and a previous geometry. Finally, a stabilization method (ES), originally proposed by Ishida, Morokuma, and Komornicki (J. Chem. Phys., 66, 2153 (1977)) and refined by Schmidt, Gordon, and Dupuis (J. Am. Chem. Soc., 107, 2585 (1985)) is used as well. It is found that to converge the FAP0 method in general requires very small step sizes (on the order of $0.001 \text{ (amu)}^{1/2}\text{-bohr}$, and that higher order methods do not result in much improvement. The ES method does converge the reaction path much more rapidly than the other methods, but this approach is more time-consuming since it requires the calculation of additional gradients. Nonetheless, the ES approach allows a much larger step size, so it may well be the method of choice.

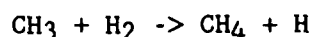
B. Ab Initio Reaction Paths and Direct Dynamics Calculations, K.K.

Baldrige, M.S. Gordon, R. Steckler, and D.G. Truhlar, J. Phys. Chem., 93, 5107 (1989).

As an extension of the work described in (A) above, several much more sophisticated algorithms for determining reaction paths and generating reaction path hamiltonians have been investigated. The algorithms analyzed include stiff methods, predictor-corrector methods, multi-step methods, and variable step size methods, in comparison with the simpler schemes discussed in the earlier paper. It has been determined that the simplest method of choice is that referred to earlier as ES2 (modified stabilization method), but that this can break down for reaction paths which are either very flat or which have parameters with widely

varying time constants. In the both cases, it is recommended that one of two methods be used: fourth order Runge-Kutta (RK4) or the local quadratic approximation (LQA) recently proposed by Page and McIver and modified and implemented in this laboratory.

To illustrate the interface of GAUSSIAN82 with the variational transition state theory code (POLYRATE) the free energy path for the reaction



was obtained and the reaction dynamics investigated. Although this calculation was performed at a rather low level, it does illustrate the power of combining electronic structure and dynamics calculations.

C. Test of Extended Basis Sets For Third Period Elements, J. Heitzinger and M.S. Gordon, J. Phys. Chem., 91, 2353 (1987).

The prediction of very accurate energetics for chemical processes generally requires at least triply split basis sets, augmented by polarization functions. For hydrogen and second period elements, the 6-311G basis, developed with correlated wave functions, has proven to be very useful for this purpose; however, there is no analogous Pople basis set for the third period elements. We have been using a triply split basis set developed by McLean and Chandler (MC) for these elements and have now tested this basis set by using it, augmented by appropriate polarization functions and combined with full fourth order perturbation theory, to predict heats of formation of third period hydrides. The very gratifying result is that the MC basis predicts these heats of formation with an accuracy equivalent to those predicted using 6-311G for the second period hydrides.

D. Basis Set Development, M.W. Schmidt, T.L. Windus, and M.S. Gordon, research in progress.

It is important to extend many of the investigations in progress or completed by this group to main group atoms in the fourth and fifth rows of the

periodic table. Unfortunately, no systematic efficient basis sets exist for these elements beyond 3-21G*. We are, therefore embarking on a systematic development of 6-31G(d) and 6-311G(d) basis sets for these elements, starting from the generally contracted basis sets developed by Dunning and co-workers.

Related to the foregoing is the continuing development of correlation-balanced basis sets. It has been shown that more polarization functions are required on hydrogen than on second period elements, X, in order to properly dissociate X-H bonds. This analysis is now continuing with analyses of third period atoms. Preliminary results suggest that if elements in the first three periods are to be treated on an equivalent footing, standard basis sets should contain p polarization functions on H and d polarization functions on third period elements. Additional basis functions should then be added to this standard basis in a balanced manner.

E. Non-Adiabatic Coupling Matrix Elements, S. Koseki, J.A. Boatz, and M.S. Gordon, research in progress.

A proper understanding of potential energy surfaces for chemical reactions frequently necessitates the computation of spin-orbit and/or vibronic coupling matrix elements. Several examples for which the former may be important have already been discussed (e.g., reactions of ^3Si with water, methane, and silane, and the reaction of silylene with molecular oxygen), and vibronic interactions are almost always important in studies of excited singlet and triplet states. Several of the routines necessary for the computation of spin-orbit coupling matrix elements have already been coded into our GAMESS program. The evaluation of vibronic coupling matrix elements requires more sophisticated MCSCF techniques than are presently available in GAMESS. To solve this problem, J.A. Boatz spent a month in the laboratory of Professor J. Amloff for the purpose of acquiring his very sophisticated MCSCF program and learning the methodology. The appropriate vibronic coupling matrix elements have now been coded into Amloff's program, and the code is being tested. Eventually, the best pieces of

the two programs will be melded into one.

F. Development of the GAMESS Computer Code, M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S. Koseki, M.S. Gordon, S.T. Elbert, and B.T. Lam, QCPE, 7, 115 (1987).

The General Atomic and Molecular Electronic Structure System (GAMESS) has become one of the most sought after quantum chemistry programs. Originally written by Dupuis, Spangler and Wendoloski (NRCC Software Catalog Program QG01, 1980), the code was taken over by the NDSU Quantum Chemistry Group (with continuing support from AFOSR), in collaboration with S.T. Elbert at Iowa State and B. Lam at Ottawa. Now available at most of the National Science Foundation Supercomputer Centers and in IBM, CRAY, SCS, VAX, CDC, and UNIX versions, GAMESS is an electronic structure program which is capable of predicting:

1. the molecular and electronic structure of molecules;
2. transition states and barrier heights for chemical reactions;
3. minimum energy paths (IRC's) for chemical reactions;
4. vibrational frequencies and normal modes;
5. Franck-Condon factors and oscillator strengths;
6. various molecular properties, including
 - a. dipole, quadrupole, and octopole moments,
 - b. electrostatic potentials,
 - c. electric field and electric field gradients,
 - d. virial theorem,
 - e. electron density and spin density,
 - f. Mulliken and Lowdin populations,
7. localized molecular orbitals by the Boys method.

The development and implementation of several other features are currently in progress. These include the computation of vibronic and spin-orbit coupling matrix elements, the calculation of analytical second derivatives of the energy, and interfacing with the dynamics program POLYRATE for the prediction of

reaction rates. The vectorization of the code is also in progress.

The computations are made using ab initio quantum mechanical methods, using gaussian orbital basis sets of sizes varying from minimal to near Hartree-Fock. Wave functions may be of the RHF, UHF, ROHF, GVB, MCSCF, or CI type, with analytical energy gradients available for all but the latter.

F. Modifications of GAUSSIAN82 and GAUSSIAN86, K.K. Baldridge and M.S. Gordon.

As noted above, GAUSSIAN82 has been modified to facilitate its interface with POLYRATE. The most important modification is the addition of the IRC codes, so that the minimum energy path for a chemical reaction can be generated with wavefunctions correlated using perturbation theory. Related to this is the automation of the scaling all correlation (SAC) method. This is a procedure developed in this laboratory for scaling the correlation energy obtained with perturbation theory. These addition of these modifications to GAUSSIAN86 is nearing completion.

G. Normal Mode Decomposition, J.A. Boatz and M.S. Gordon, J. Phys. Chem., 93, 1819, (1989);

Normal mode vibrations, like delocalized molecular orbitals, are often difficult to interpret for complicated molecules, because they are symmetry adapted and therefore couple the motions of several local internal motions. We have developed a method for transforming the normal mode frequencies into "intrinsic" frequencies for local internal coordinates. These are intuitive values which are consistent with "chemical" expectations. For example, the CC stretching frequencies increase in the order ethane < benzene < ethylene < acetylene. The benzene value would be particularly difficult to extract from the standard normal modes. In the first paper, the method is presented and applied to some relatively simple systems. Subsequent studies will apply the method to complicated fused ring compounds.

H. Analysis of the Vibrational Frequencies Along the $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ Reaction Path, J.A. Boatz and M.S. Gordon, J. Phys. Chem., 93, 5774 (1989).

As an illustration of an important use of the vibrational decomposition scheme described above, the transverse normal modes along the $\text{CH}_3 + \text{H}_2$ reaction path were decomposed into their internal coordinate contributions. This provides a valuable insight into those internal motions which are coupled with each other and with the reaction path.

I. Prediction of Heats of Formation for Alkylsilanes, J.A. Boatz, M.S. Gordon, and R. Walsh, J. Phys. Chem., 93, 1584 (1989).

The heats for the appropriate homodesmotic reactions, evaluated at the MP2/6-31G(d,p) level of computation, can be combined with experimental heats of formation of reference compounds to predict heats of formation which are not known experimentally. This method has been applied to several cyclic and acyclic alkylsilanes with considerable success. For the acyclic compounds, the predicted heats of formation are in good agreement with most experimental values. Where there is disagreement, additivity relations suggest that theory is correct. For the cyclic compounds, the predicted heats of formation provide the first reliable estimates.

V. SILYLENES

A. Potential Triplet Silylenes, M.W. Schmidt and M.S. Gordon, Chem. Phys. Lett., 132, 294 (1986).

The ground state of silylene is a singlet, in contrast with the triplet ground state of the carbon analog, methylene. It is well known that the chemistry of such species is dramatically altered by the electronic state, so it is of interest to determine which substituents might stabilize either the singlet or the triplet. There are two ways in which one might expect to preferentially stabilize a triplet silylene, SiR_2 . When the R-Si-R angle opens to 180° , the triplet state lies below the singlet, so one expects that the

introduction of a bulky enough substituent will open the angle sufficiently to force the triplet below the singlet. For R=methyl and t-butyl, this angle opening is apparently not large enough, since the singlet remains the ground state, although the splitting between the two states is estimated to drop from 18 to 10 kcal/mol in the case of di-t-butylsilylene.

The second approach to design a triplet silylene is to introduce electropositive substituents, since the introduction of electronegative substituents has the opposite effect in the analogous carbon compounds. Indeed, the dilithio compound has a triplet ground state. In fact, there are two low-lying triplet states. One of these is the expected linear 3B_1 structure. Even lower in energy, however, is an unusual, highly bent 3A_2 structure which may be interpreted as a weakly bound complex between silicon atom and diatomic lithium. The companion 1A_2 state is about 1 eV higher in energy and has a similar structure. Because the A_2 states are far from pure spin states in the UHF approximation, the most reliable calculations are those at the SOCI/FORS MCSCF level, with the 6-31G(d) basis set. Note that the corresponding A_2 states are predicted to be relatively much higher in energy in the parent silylene.

B. (SiH₃)₂Si, D. Bartol and M.S. Gordon, J. Am. Chem. Soc., 109, 5948 (1987).

Because the lithium substituent discussed above may not be experimentally realistic, we have investigated the electropositive silyl group as an alternative for producing a triplet ground state. While the desired effect of preferentially lowering the triplet state is indeed observed, the ground state of this species is still a singlet, although only by a predicted 6 kcal/mol. Isomers of disilylsilylene include trisilacyclopropane and the silicon analog of propene. In the carbon analog, of course, the global minimum on the singlet surface is propene. In contrast, we find the global minimum on the singlet Si₃H₆ surface to be the cyclopropane analog.

C. SiH₃-Si-Li, M.S. Gordon, research in progress.

This molecule is expected to have a triplet ground state, since several groups have predicted HSiLi to be a triplet. Both the singlet and triplet surfaces appear to have interesting features. So far, we have found two minima on the singlet surface at the SCF/6-31G(d) level of theory, a closed shell $^1A'$ (C_s) structure with a Si-Si-Li angle of 94° and an open shell 1A (C_1) structure with an angle of 147° . The latter is more than 10 kcal/mol lower than the former at the SCF level, but this could change when correlation corrections are added. The $^3A''$ state appears to be the global minimum and has an Si-Si-Li bond angle of 147° , while the $^3A'$ state is unstable and falls apart to SiH₃Si + Li.

D. Potential Energy Surfaces of Silylene, S. Koseki and M.S. Gordon, J. Molec. Spectrosc., 123, 399 (1987).

This work was initiated as a collaborative endeavor with J. Steinfeld at M.I.T. and was a direct outgrowth of an interaction which developed at the 1985 AFOSR contractor's meeting. Two dimensional MCSCF/6-31G(d,p) potential energy surfaces were calculated for the three lowest-lying states of SiH₂: 1A_1 , 1B_1 , and 3B_1 . The seam of common energy for the 1A_1 ground state and the 3B_1 state is found to lie very close to the 3B_1 minimum. Indeed, the zero point vibrational energy of that species is more than sufficient to enable it to cross the seam from its minimum; thus, one expects fast radiationless transitions to occur from the triplet to the ground state singlet. The transition dipole length and velocity connecting the two singlet states exhibit a strong dependence on the normal coordinates. Although these two measures of oscillator strength differ from each other quantitatively, they exhibit the same trends. The vibrational structure of the absorption spectrum from the 1A_1 state to the 1B_1 state calculated by using the dipole length as a simple function of the normal coordinates is similar to that obtained within the Franck-Condon approximation. It is especially gratifying that Steinfeld used our oscillator strengths to estimate a lifetime for the (0, 2, 0) vibrational level of the 1B_1

state which is in good agreement with experiment.

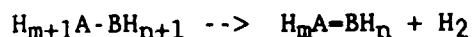
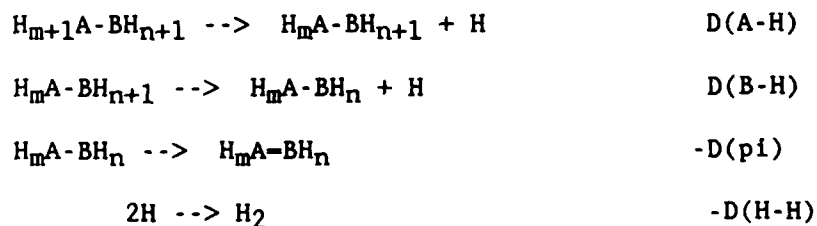
E. Heats of Formation of Methylsilylene and Dimethylsilylene, J.A. Boatz and M.S. Gordon, *Organomet.*, 8, 1978 (1989).

As part of a three-part series of papers on silylene heats of formation (in collaboration with M.A. Ring and R. Walsh) isodesmic reactions were used to predict the heats of formation for Methylsilylene and dimethylsilylene. The predicted values are in excellent agreement with the experimental values.

VI. PI BONDING

A) Pi Bond Strengths in the Second and Third Periods, M.W. Schmidt, P. Truong, and M.S. Gordon, *J. Am. Chem. Soc.*, 109, 5217 (1987).

In this series of calculations, all possible pi bonds formed between the elements C, N, O, Si, P, and S were estimated in two ways. Where possible, the pi bond strength was obtained from the barrier to internal rotation; that is, by rotating one end of the molecule by roughly 90° in order to break the bond. Because this process creates a diradical, it must be studied using MCSCF wave functions. Some molecules, such as H₂CO, cannot be studied in this manner, since one end of the molecule (the oxygen end in this case) has no "handle". Therefore, the pi bonds in all molecules were also investigated using the following thermodynamic cycle:



This approach requires the knowledge of the A-H and B-H bond energies, but MCSCF wave functions are not required. All geometries were optimized using the 3-21G* basis set. For the internal rotation calculations, the 6-31G(d) basis set was used, and the FORS MCSCF wavefunctions were augmented by second order

configuration interaction (SOC) calculations at the MCSCF geometries. For the thermodynamic cycles, single point energies were obtained with fourth order (MP4) perturbation theory and the MC-311G(d,p) basis set. It is particularly gratifying that the methods agree very well with each other for the prediction of pi bond strengths. We find that the ability of the aforementioned elements to form pi bonds is in the order $O > N = C \gg S > P > Si$. The general trend can be explained by the very strong reluctance of third period atoms to hybridize, combined with the decreased pi bonding ability in that period.

B. The Electronic and Molecular Structure of Silicocene, K.K. Baldrige, M.S. Gordon, and J. Corey, unpublished results.

Silicocene, the silicon analog of the iron sandwich compound ferrocene, was isolated and its crystal structure reported by Jutzi et al (Angew. Chem., 25, 164 (1986)). There are apparently two structures for this species, one in which the two cyclopentadienyl rings are coplanar in a D_{5h} arrangement and one in which the two rings are slightly tilted relative to each other. The two structures are reported to occur in a 1:2 ratio. A restricted Hartree-Fock (RHF) geometry optimization was carried out on the D_{5h} compound using the 3-21G* basis set. At this level of theory, it is found that the D_{5h} structure is not a potential energy minimum. Rather, there is a pair of degenerate imaginary frequencies ($96i \text{ cm}^{-1}$), corresponding to degenerate bending motions of the two rings away from coplanarity. An even smaller (real) frequency of 10 cm^{-1} corresponds to the internal rotation of the two rings. If these calculations are correct, this suggests that the more symmetric structure reported experimentally is stabilized in the crystal by crystal forces. Since silicocene is an unusual silylene, the nature of its bonding is of interest. Boys localized molecular orbitals predict that there is a silicon lone pair which is almost purely 3s in character and (pi) bonds from the silicon to each carbon which are highly polarized toward the carbons. The next step in this study is to fully optimize the less symmetric

structure.

C. Potentially Aromatic Metalloccycles, K.K. Baldrige and M.S. Gordon, J. Am. Chem. Soc., 110, 4024 (1988).

The concept of "aromaticity" (perhaps more properly referred to as ring delocalization stabilization) is a somewhat arbitrary one, but a quantitative measure of the stabilization of a cyclic compound due to delocalization of the pi electron density may be obtained using "isodesmic" reactions. These are reactions in which each formal bond type is conserved, the advantage being that computational errors at the Hartree-Fock level are minimized. Two particular types of isodesmic reaction, bond separation reactions and superhomodesmotic reactions, are particularly useful for the present purposes. In a bond separation reaction the aromatic ring (e.g., benzene) is broken into its smallest component parts (e.g., three ethanes and three ethylenes) in a properly balanced reaction. The reaction enthalpy then measures the stabilization relative to these components. The disadvantage to this approach is that the resultant stabilization arises not only from the ring structure, but also from the ordinary conjugation of alternating single and double bonds. Superhomodesmotic reactions overcome this difficulty (at the expense of much greater amounts of computer time) by relating the parent ring compound to a conjugated molecule of the same size (e.g., 1,3,5-hexatriene).

In this study both types of reaction are being used at the RHF/3-21G* level to probe the "aromaticity" of C, Si, Ge, Sn, N, P, As, and Sb in six-membered rings and of N, P, As, Sb, O, S, Se, and Te in five-membered rings. As expected, the energy differences are much smaller for the superhomodesmotic than the bond separation reactions, since there is a much smaller change on going from reactants to products in the former. However, the trends observed for the two types of reactions are essentially the same. For example, silabenzene is found to be about 70% as aromatic as benzene, while the corresponding value is roughly 88% for phosphorus vs. nitrogen. Replacing Si

with Ge or P with As in the six-membered rings has very little effect on the stabilization, according to the bond separation reactions, with the corresponding ratios being 98% and 94%, respectively. Continuing this trend, Sb is almost as effective as As in stabilizing the metallobenzene, whereas stannobenzene is only two thirds as aromatic as germabenzene. The corresponding superhomodesmic reactions are currently under investigation for the fourth and fifth period atoms. In the five-membered rings a dramatic drop in stabilization is observed on going from N to P. Indeed, the superhomodesmic reaction predicts the phosphorus compound to be less stable than its acyclic analog. On the other hand, the order of stabilization for the group VI elements is $S > Se > O, Te$. This is related to the strain in the oxygen ring relative to the other group VI five-membered rings and is in good agreement with available experimental rate data.

D. Substituted Silabenzenes, K.K. Baldridge and M.S. Gordon, Organometallics, 7, 144 (1988).

The effect of twelve substituents (F, OH, NH_2 , CH_3 , Cl, SH, PH_2 , SiH_3 , CN, COOH, NO_2 , and OCH_3) on the aromaticity, electronic structure, and nucleophilic directing tendencies of silabenzene has been studied at the 3-21G//STO-2G level of theory. The analogous substituted benzenes have been included for comparison. The aromatic character of these compounds has been quantified using the appropriate bond separation reactions. These suggest that, with a few exceptions, the substituents cause only minor variations in the aromatic character of benzene and silabenzene rings. Fluorine is the only substituent that increases the aromaticity of both rings. Generally, the silabenzene is roughly 80% as aromatic as benzene. The directing ability of the substituents has been probed with the use of electron density difference maps. Here, the electron density of the parent compound (benzene or silabenzene) is subtracted from the substituted compound. Using this method, it can be beautifully

demonstrated that certain substituents are ortho/para-directing, while others are meta-directing. For those substituents that are well understood for benzene, the agreement with experiment is excellent. Third period substituents are predicted to behave similarly to their second period analogs, except that the silyl group is found to be a meta director. For a given orientation of the substituent, the directing tendencies on silabenzene are predicted to be similar to those on benzene. A critical exception to this is that re-directed pi density avoids the silicon atom, so that, for example, a meta director placed meta to the silicon will not direct pi density to the silicon.

E. Hydride Abstraction from Siloles: Routes to Potentially Anti-aromatic Species, P. Boudjouk, A.B. Rajkumar, J. Lambert, W. Schilf, M.S. Gordon, and K. Nguyen, *Organomet.*, submitted.

It was demonstrated earlier that the potentially aromatic, 6 pi electron, silacyclopentadienyl anion has very little delocalization stabilization (in contrast to the hydrocarbon analog), probably because the silicon avoids any local build-up of negative charge. This work was initiated to determine if the propensity of silicon for positive charge has a similarly dramatic reduction of the anti-aromaticity in the corresponding 4 pi electron cation. This has indeed been found to be the case. Using the appropriate isodesmic reaction, relating the ring to isolated single and double bond systems, the silicon cation is actually predicted to be slightly aromatic, whereas the carbon system is anti-aromatic. Homodesmic reactions, which relate the rings to acyclic delocalized structures also show the silicon ring to be much more stable than its hydrocarbon analog.

F. Pi Bonds to Ge and Sn, T.L. Windus, K.K. Baldrige, and M.S. Gordon, research in progress.

As an extension to the previous work on pi bonding in second and third period elements, we have initiated a series of calculations to determine the pi bond strengths for multiple bonds between Ge and Sn with main group elements in

the 2nd-5th periods.

VII. STRAINED RINGS.

A. Structure and Bonding in Cycloalkanes and Silacycloalkanes, J.A. Boatz, M.S. Gordon, and R.L. Hilderbrandt, J. Am. Chem. Soc., 110, 352 (1988).

The molecular structures and vibrational frequencies for the cycloalkanes C_nH_{2n} and silacycloalkanes $SiC_{n-1}H_{2n}$ ($n=3,4,5,6$) have been predicted at the RHF/3-21G* level of theory and compared where possible with the corresponding experimental values. The predicted structures agree well with experiment, while the vibrational frequencies are generally somewhat too high as expected. Particularly for the silacycloalkanes, the predicted vibrational frequencies should prove to be a useful guide since the experimental values are less well known.

The strain of the eight rings have been predicted at the MP2/6-31G(d)//3-21G* level, using homodesmic reactions similar to those discussed above for the aromatic compounds. Agreement with experiment is within 3 kcal/mol for the carbon compounds, and this provides some confidence in the predictions for the silicon compounds where the experimental data is not available. Silacyclopropane is predicted to be rather more strained than cyclopropane, but this trend is reversed for the four-membered rings. This is largely due to the ability of silicon to accomodate bond angles in the vicinity of 90° . The same homodesmic reactions can be used to predict the heats of formation of the cyclic compounds as long as the heats of formation of the acyclic reference compounds are known experiemntally. Once again, the agreement with experiment is excellent for the carbon compounds. For the silicon molecules the heats of formation are unknown even for some of the reference compounds, and indeed we suggest, based on our calculations, that at least two experimental heats of formation (those for ethylsilane and diethylsilane) are incorrect.

B. Silabicyclobutanes and Silacyclobutenes, J.A. Boatz and M.S. Gordon, J. Phys. Chem., 92, 3037 (1988).

The structures, vibrational frequencies, and bent bond lengths are predicted for the bicyclobutanes $C_nSi_{4-n}H_6$ ($n=0-4$), and for their cyclobutene analogs. The strain energies are predicted using the appropriate homodesmotic reactions. The same reactions can be used to predict heats of formation when those of the reference compounds are known. It is found that the bonds in these compounds can be very bent, the most dramatic example being the isomer of $Si_2C_2H_6$ in which the two silicons are in the bridge positions. In this compound the internuclear distance is a very unusual 2.15 Å, whereas the bent bond length is a more "normal" single bond length of 2.3 Å. Some of the compounds, particularly the bicyclobutanes with bridging Si-Si bonds, actually have two minima, one with a normal bridgehead bond length and one with a rather stretched bridgehead bond. Because the latter is so long, preliminary calculations suggest that there is considerable diradical character. Therefore, it is not entirely clear which of the two isomers is more stable. Additional calculations are proceeding in this laboratory to determine the relative energies.

C. Three-Membered Rings, J.A. Boatz and M.S. Gordon, J. Phys. Chem., 93, 3025 (1989).

The molecular structures and vibrational frequencies for the three-membered rings C_2H_4X and Si_2H_4X have been calculated at the RHF/6-31G(d) level of theory, for $X=CH_2$, NH, O, SiH_2 , PH, S. Ring strain energies and heats of formation have been predicted at the MP2/6-31G(d)//HF/6-31G(d) level, using the appropriate homodesmotic reactions. The thermodynamics of the insertion of X into the $CH_2=CH_2$ and the $SiH_2=SiH_2$ double bonds to form the corresponding ring compounds have been calculated at the same level of theory. The strain energies and heats of formation are both within 2 kcal/mol of the experimental values where the latter are known. The insertion exothermicities are not quite as accurate, because the

reactions are not homodesmic.

Because of the extreme sensitivity of the electron density to basis set in many of these three-membered rings, we have found that the bent bond analysis must be carried out with a basis set which contains at least two sets of d orbitals on the ring atoms. Otherwise, spurious maxima and minima appear along a bond. The bent bond analysis is very revealing. The internuclear base bond internuclear distances are found to decrease considerably as the electronegativity of the apex group is increased. This is accompanied a planarization of the base C_2H_4 or Si_2H_4 moiety. This has led some authors to suggest that the structure of these three-membered rings is becoming more and more like a pi complex between the apex group and the X_2H_4 moiety. However, the bent bond analysis clearly shows that the actual (bent) bond lengths are the same as those expected for normal single bonds, and no double bond character is apparent. This is verified by Mulliken population analyses which show little pi overlap for either the C-C or Si-Si bonds.

D. Inversion and Isomerization in Bicyclobutane, M.S. Gordon, J.A. Boatz, and K.A. Nguyen, research in progress.

There have been several previous theoretical papers which dealt with the inversion motion of bicyclobutane; however, none of them were definitive. Several were carried out with semi-empirical methods, all assumed the motion occurs through a planar d_{2h} transition state, and only the most recent paper actually calculated the hessian at the supposed transition structure. Unfortunately, that most recent paper was performed at the SCF level, thereby rendering the calculation useless, since the transition state is a diradical. We have performed full geometry optimizations withh GVB/6-31G(d) wavefunctions. At this level of theory, the D_{2h} structure has two imaginary frequencies, so it is not a transition state. In fact, the transition state has C_{2v} symmetry, the reaction being an asynchronous narcissistic reaction. The introduction of a multi-configurational treatment lowers the calculated barrier by nearly 50

kcal/mol relative to the RHF treatment.

The isomerization of bicyclobutane to butadiene has also been the subject of considerable experimental and theoretical interest. We have initiated an extensive MCSCF study of the isomerization potential energy surface in order to determine if this is a concerted or two-step mechanism. Subsequently, the dynamics of the isomerization will be investigated.

E. Bond Stretch Isomerism in Silabicyclobutanes, J.A. Boatz and M.S. Gordon, J. Phys. Chem., 93, 2888 (1989).

It has been discovered by us and others that tetrasilabicyclobutane exists as two isomers which differ primarily in the length of the bridge bond. We have found that when silicon atoms are in the bridgehead positions, the "bond stretch" isomer is lower in energy. In this work, the transition states connecting the two isomers have been determined for tetra-, tri- and di-silabicyclobutane, using GVB/3-21G* wavefunctions. Relative energies and barrier heights were obtained at the GVB/6-31G(d) level. In each case, the minimum energy path connecting the transition state with the isomers has been determined. The most interesting result is that disilabicyclobutane has two transition states connecting the same pair of isomers. The lower energy transition structure corresponds to an inversion of the four heavy atoms, as well as a stretching of the bridge bond.

VIII. UNUSUAL BONDING ENVIRONMENTS

A. The Molecular Structure of Two SilylAzides, R. West, S. Zigler, and M.S. Gordon, Organomet., 8, 1656 (1989).

The crystal structure for two highly substituted silyl azides (R_3SiNNN) have recently been determined by West and co-workers. In contrast to the methyl analog, they find that the inner NN bond is actually slightly shorter than the terminal NN bond in one of the compounds. For the carbon compound, we find the terminal and inner NN bond lengths to be 1.102 and 1.228Å, respectively, at the

RHF/6-31G(d) level of theory. Using the same basis set and MP2 geometry optimizations, these values become 1.163 and 1.243 Å. In the silicon case, the RHF bond lengths are 1.099 and 1.221 Å, respectively. While each of the bonds is slightly shorter than in the carbon compound, the bond length difference is essentially the same. The MP2/6-31G(d) bond lengths in the silicon compound are 1.173 and 1.229 Å, respectively. While the two bond lengths are closer to each other here than they are in the analogous calculation for the carbon compound, there is still a significant difference between theory and experiment. Increasing the basis set size to MC-311G(d) has little effect. This leaves three possible solutions: (1) Higher levels of theory are needed to obtain the correct bond lengths. If this is the case, it is likely that either fourth order perturbation theory or an MCSCF is needed to incorporate triple or higher substituions; (2) The substituents on the experimental compound have an unusually large effect on the structure; (3) There is a large disparity between the gas phase and crystal structures. Of course, all three possibilities may contribute.

B. The Electronic and Molecular Structure of Silyl Nitrene, M.S. Gordon, Chem. Phys. Lett., 146, 148 (1988).

The photolysis of silyl azides results in the elimination of molecular nitrogen and the ultimate formation of a silaimine. An interesting question regarding the primary process is whether the silyl nitrene, R_3SiN , is formed as an intermediate. As a first step in answering this question, the molecular and electronic structure of silyl nitrene has been investigated in its lowest singlet and triplet states. The ground electronic configuration is $(e)^2$. This gives rise to 3A_2 , 1E , and 1A_1 states, and one expects the triplet to be the ground state. Using FORS MCSCF geometries with the 6-31G(d,p) basis set, augmented with second order CI for energetics, the triplet is not only predicted to be 1.8 eV below the 1E state, but just 8 kcal/mol above singlet silaimine. This is in contrast with the methyl analog in which the triplet nitrene is 46

kcal/mol above the singlet imine.

C. Isomers of HSiNO, M.S. Gordon and P. Gaspar, research in progress.

Gaspar and co-workers have been conducting experiments in which they hope to isolate compounds with the formula RSiNO, and the speculation is that a likely structure is a cyclic one with the hydrogen bonded to the silicon. We have embarked on a theoretical study of isomers of this species in the lowest singlet and triplet states, using MP4/6-31G(d,p) energies at the HF/6-31G(d) geometries. For the singlet surface:

(1) So far the global minimum appears to be linear H-N-Si-O, at the MP4 (SDTQ)/6-31G(d,p) level of theory.

(2) H-N-O-Si closes to a silylene ring, which is 23.7 kcal/mol higher than (1) at the same level of theory.

(3) H-O-N-Si is nonplanar and 29.4 kcal/mol above (1).

The foregoing all have stable wavefunctions and are well-behaved. In addition,

(4) H-Si-N-O is nearly planar, nearly linear at the nitrogen, and 52.1 kcal/mol above (1). The RHF solution for this isomer is unstable, so further calculations are needed, but it's unlikely to be energetically competitive with (1).

(5) As mentioned earlier the H-SiNO ring opens at the NO bond to form a diradical. This is estimated to be more than 60 kcal/mol above (1).

(6) The isomer H-Si-O-N has so far resisted SCF convergence.

For the triplet surface:

(7) H-N-Si-O is 50.9 kcal/mol above (1).

(8) H-Si-N-O is 69.6 kcal/mol above (1) and 17.5 kcal/mol above (4).

(9) Cyclic H-Si-O-N is 74 kcal/mol above (1), but very close in energy to its singlet analog, the diradical (5).

(10) H-Si-O-N is 76.3 kcal/mol above (1).

D. Allene Analogs, M.S. Gordon, M.W. Schmidt, and S. Koseki, *Inorg. Chem.*, **28**, 2161 (1989).

It is well known that the structure of allene, $\text{CH}_2=\text{C}=\text{CH}_2$, is such that the two CH_2 groups are twisted by 90° relative to each other. This occurs because the p orbitals used in the pi bond on one end are orthogonal to those used in the pi bond on the other end. Carbodiimides, e.g., $\text{HN}=\text{C}=\text{NH}$, behave similarly, with the two NH groups approximately twisted by 90° degrees relative to each other. It has been noted by Thomson and Glidewell, however, that disiladiimide is actually planar. Michl has found similar behavior for substituted disiladiimides using MNDO calculations. No speculations were put forward to explain this apparently anomolous behavior, so this investigation was initiated. Recall that the Si-N pi bond is much weaker than that in C-N. This should mean that it will be easier to twist the silicon structure to planarity than the carbon structure. On the other hand, in the planar structure the nitrogen lone pairs can delocalize into the pi system. This combination of phenomena, verified by the analysis of localized orbitals for these structures, apparently leads to a planar structure for disiladiimide. In fact, analysis of the entire surface, not performed by previous investigators, reveals that it is very flat and that the preference for any structure is actually very flat. One might speculate that other weak pi bonds might behave similarly. One possibility therefore is $\text{HP}=\text{Si}=\text{PH}$. Investigation of this compound, however, yields a predicted structure which is consistent with allene. This is, in fact, consistent with the calculations of Schleyer and co-workers who have noted that phosphorus does not easily share its lone pairs. Indeed, the localized orbital analysis demonstrates the P lone pairs to be nearly pure, in contrast to those on N.

Our conclusion is that the structure of such compounds is a balance between the strength of the pi bonds on the one hand (favoring the twisted form) and the delocalization capability of the terminal lone pairs on the other hand (favoring

the planar structure). In siladiimide, the balance is very close, and this leads to a very flat potential energy surface.

E. Structures and Relative Energies of CNSiH_m Compounds ($m=3,5,7$), P.

Truong, T.N. Truong, and M.S. Gordon, in preparation.

Because of the importance of the Si-C-N linkage in composites and bioactivity, a systematic investigation has been carried out on the simplest sequence of such compounds, using MP4/6-31G(d)//HF/3-21G(d) energies. For $m=3$, the minimum energy structure of the 13 isomers studied is silyl nitrile (SiH_3CN), followed closely by CH_3NSi (4.6 kcal/mol higher) and silyl isonitrile (6.6 kcal/mol). All remaining isomers are at least 25 kcal/mol higher in energy. For $m=5$, the minimum energy isomer of the 13 investigated is predicted to be methylaminosilylene ($\text{CH}_3\text{-Si-NH}_2$). The closest isomer ($\text{SiH}_3\text{N=CH}_2$) is already 15 kcal/mol higher in energy. For $m=7$, the lowest energy isomer is predicted to be $\text{CH}_3\text{-SiH}_2\text{-NH}_2$.

H. Structures of Neutral Pentacoordinated Compounds, M.S. Gordon, L.P. Davis, and L.W. Burggraf, Chem. Phys. Lett., in press.

In an attempt to hypervalent bonding of silicon in uncharged environments, we have undertaken a series of ab initio and semi-empirical calculations on neutral compounds containing pentacoordinated silicon. So far, all molecules investigated have an ammonia molecule and an electronegative atom in the axial positions. Generally, these compounds are only slightly more stable than the separated components (NH_3 + a tetrahedral silane). This is best illustrated by the computed Si-N bond lengths. These are (in parentheses) for F axial and H equatorial (2.818 Å), Cl axial and H equatorial (2.780), Cl axial and Cl equatorial (3.488), and Cl axial, F equatorial (2.153). For comparison, the Si-N bond length in silylamine is 1.725 Å. The binding energies in these compounds, relative to the silane plus ammonia, are in the 5-10 kcal/mol range. We are now in the process of carrying out similar studies of the more complicated silatrane compounds.

PUBLICATIONS

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